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Effect of Zr/Ti ratio on piezoelectric and dielectric properties of PNW–PMS–PZT ceramics

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Abstract $(Pb_{0.95}Sr_{0.05})[(Ni_{1/2}W_{1/2})_{0.02}(Mn_{1/3}Sb_{2/3})0.06(Zr_XTi_Y)_{0.92}]O_3$ piezoelectric ceramics (abbreviated as PNW–PMS–PZT) with 1%mol excess PbO, 0.25 wt% CeO_2 and 0.2 wt% MnO_2 were prepared by traditional ceramics process. The phase structure of ceramics sintered at 1150°C were analyzed. Results show that the pure perovskite phase was in all ceramics specimens, the phase structure of PNW–PMS–PZT piezoelectric ceramics was transformed from tetragonal to rhombohedral, with Zr/Ti ratio increased in system; Effect of Zr/Ti ratio on piezoelectric and dielectric properties was investigated. Results show that ε_r, $tan\delta$, k_p and d_{33} increased with an increase of Zr/Ti ratio and reached the maximum values at Zr/Ti ratio of 50/50, then decreased with further increase of Zr/Ti ratio, whereas the variation of Q_m with an increase of Zr/Ti ratio showed the opposite trend, T_c showed a tendency to decrease with an increase of Zr/Ti ratio. The piezoelectric ceramics with Zr/Ti ratio of 50/50 was applied in high-power multilayer piezoelectric transformer, and properties parameter were ε_r= 2100, $tan\delta$=0.006, k_p=0.613, Q_m=1300, d_{33}=380pC/N, T_c=205 °C.

Keywords PNW–PMS–PZT ceramics · Piezoelectric transformer · Piezoelectric properties · Zr/Ti ratio

1 Introduction

Piezoelectric ceramics $Pb(Mn_{1/3}Sb_{2/3})O_3$–$Pb(Ti, Zr)O_3$ (abbreviated as PMS–PZT) is a promising candidate for piezoelectric transformer because of its significantly higher electromechanical coupling factor k_p, larger mechanical quality factor Q_m and higher maximum vibration velocity than PZT [1–3]. However, PMS–PZT have some disadvantages such as lower dielectric constant ε_r (660) and higher sintering temperature (1250 °C) [4, 5]. Piezoelectric transformer should have a high output current to increase its output power. At the same time, in order to achieve a piezoelectric transformer with a high output current, its output capacitance must be high. Therefore, the piezoelectric ceramics for high-power piezoelectric transformers must have higher dielectric constant ε_r [6, 7]. In addition, the sintering temperature of about 1250 °C may be a serious problem for high-power mutilayer piezoelectric transformer. $Pb(Ni_{1/2}W_{1/2})O_3$ (abbreviated as PNW) exhibits a very broad peak and a low sintering temperature [8]. Gao et al. have reported that PNW–$PbTiO_3$ have large dielectric constant and low sintering temperature (970 °C) [9]. Juhyun Yoo et al. have reported that PNW–$Pb(Mn_{1/3}Nb_{2/3})O_3$–PZT ceramics have larger dielectric constant and lower sintering temperature than $Pb(Mn_{1/3}Nb_{2/3})O_3$–PZT ceramics [6].

In our previous study, the effect of PMS and PNW on phase structure, piezoelectric and dielectric properties of PNW–PMS–PZT ceramics was investigated in detail [7]. The purpose of this paper is to investigate the effect of sintering temperature and Zr/Ti ratio on microstructure and

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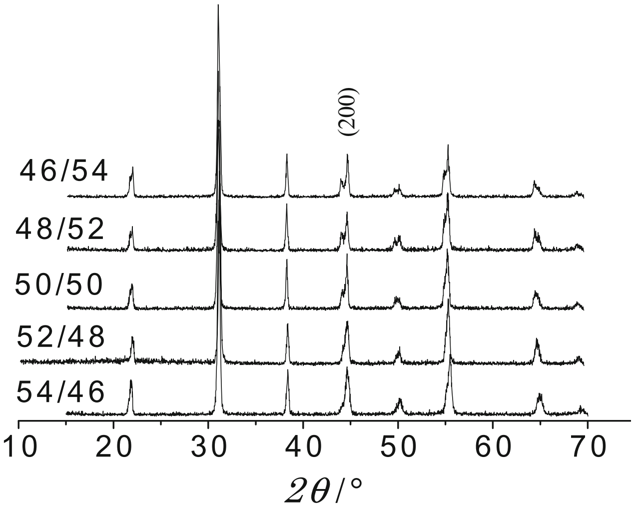

Fig. 1 XRD patterns of the specimens sintered at 1150 °C as function of Zr/Ti ratio

properties of PNW–PMS–PZT ceramics, and to find promising candidates for high-power mutilayer piezoelectric transformer.

2 Experimental procedure

The specimens studied in this study were fabricated according to formula: $(Pb_{0.95}Sr_{0.05})[(Ni_{1/2}W_{1/2})_{0.02}(Mn_{1/3}Sb_{2/3})_{0.06}(Zr_xTi_y)_{0.98}]O_3$+0.25wt%($CeO_2$)+1%mol excess (PbO)+0.2%wt(MnO_2), where x/y=46/54, 48/52, 50/50, 52/48, 54/46 respectively, The specimens were prepared by traditional ceramics process and reagent-grade Pb_3O_4, ZrO_2, TiO_2, $SrCO_3$, NiO, WO_3, MnO_2, Sb_2O_3 and CeO_2 powders were acetone-milled for 12 h in a zirconia ball mill and then calcined at 850°C for 2 h. The calcined powders were ground, ball-milled again and pressed into disks using PVA as a binder. After burning off PVA, the pellets were sintered in a sealed alumina crucible at different soaking temperature (from 1075 to 1200 °C) for 2 h. In order to compensate for PbO loss from the pellets, a PbO-rich atmosphere was maintained by placing an equi-molar mixture of PbO and ZrO_2 inside the covered alumina crucible.

The phase structure of the sintered ceramics was analyzed by using a Rigaku D/Max-2400 diffractometer using Cu Kα radiation. The fractured surfaces were examined by scanning electron microscopy (HITACHI S-2700). The specimens were polished for the dielectric and piezoelectric studies. Silver paste was fired on both sides of the samples at 560 °C for 10 min as the electrodes for the dielectric and piezoelectric measurements. The dielectric response was measured at the frequency of 1 kHz using an automatic LCR meter (WK4225) at a temperature range from 50 °C to 450 °C. The samples were poled in 120 °C silicon oil bath by applying a DC electric field of 3 kV/mm

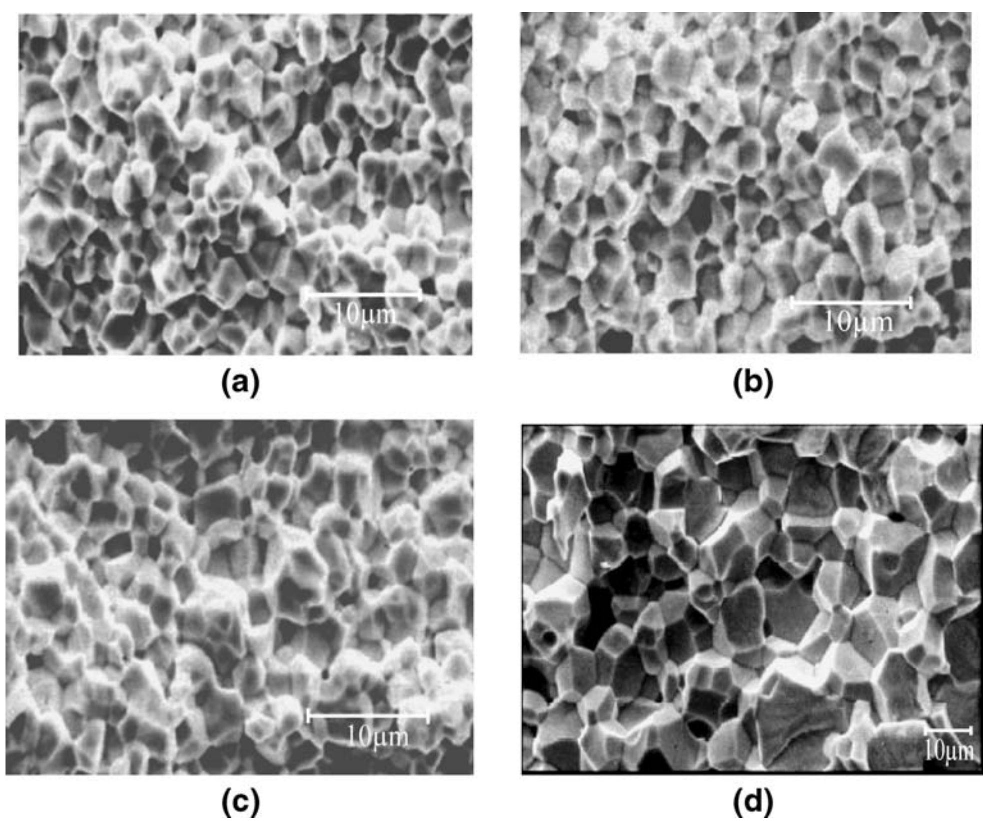

Fig. 2 SEM photographs of the fractured surface of the specimens with Zr/Ti ratio of 50/50 as function of the sintering temperature: (**a**) 1075 °C, (**b**) 1100 °C, (**c**) 1125 °C, (**d**) 1150 °C

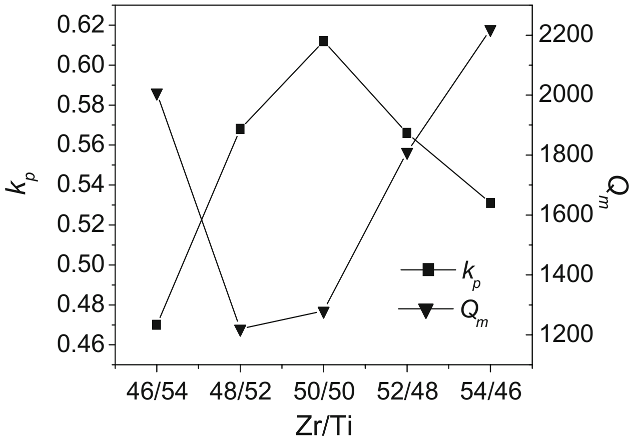

Fig. 3 k_p and Q_m of PNW–PMS–PZT ceramics with the different Zr/Ti ratio

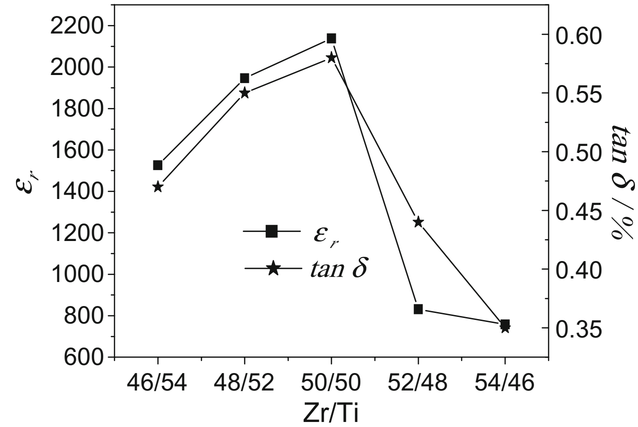

Fig. 5 ε_r and *tanδ* (1 kHz) of PNW–PMS–PZT ceramics with the different Zr/Ti ratio

for 30 min. The specimens were aged for 24 h prior to testing. Piezoelectric properties were measured by the resonance-antiresonance method on the basis of IEEE standards using an impedance analyzer (HP4294A).

3 Results and discussion

3.1 Phase analysis

Figure 1 shows X-ray diffraction patterns of specimens sintered at 1150 °C as function of Zr/Ti ratio. Only pure perovskite phase exists and no detectable trace of the pyrochlore structure can be found. It is noted that the peak splitting at (2 0 0) plane position weakens gradually as Zr/Ti ratio increased. It is reported that tetragonal and rhombohedral phases were identified by an analysis of the peaks (0 0 2) and (2 0 0) in the 2θ range of 43–47 °C [10, 11]. The splitting of (0 0 2) and (2 0 0) peaks indicates that they are the ferroelectric tetragonal phase (F_T), while the single (2 0 0) peak shows the ferroelectric rhombohedral phase (F_R).

Figure 2 shows the SEM micrographs of the fractured surface of the specimen with Zr/Ti ratio of 50/50 sintered from 1075 to 1150 °C for 2 h. When sintering temperature increased, grain size and densification were increased simultaneously. At 1150 °C in Fig. 2(d), a very homogeneous and pore-free structure can be seen. The grain size is about 9.6 μm for PNW–PMS–PZT ceramics sintered at 1150 °C.

3.2 Piezoelectric properties

Besides the change in microstructure, Zr/Ti ratio also affects the piezoelectric properties of PNW–PMS–PZT ceramics. Figure 3 shows k_p and Q_m as a function of Zr/Ti ratio. It is observed in Fig. 3 that as the Zr/Ti ratio increases, value of k_p represents a peak of 0.613 at Zr/Ti ratio of 50/50, when Zr/Ti ratio is further increased, value

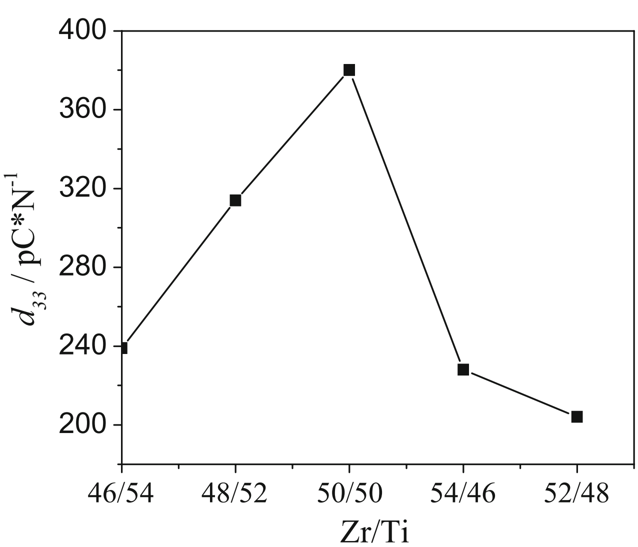

Fig. 4 d_{33} of PNW–PMS–PZT ceramics with the different Zr/Ti ratio

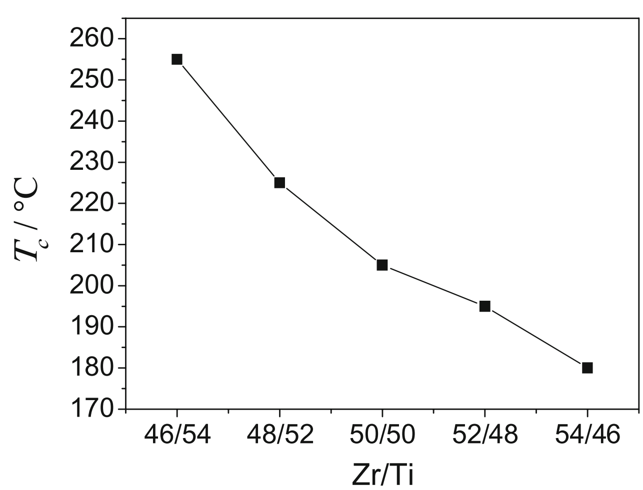

Fig. 6 T_c of PNW–PMS–PZT ceramics with the different Zr/Ti ratio

of k_p decrease. Q_m continues to decrease and finally it shows the minimum value when Zr/Ti ratio is 48/52. This is duo to fact that the phase structure of PNW–PMS–PZT ceramics changes from the tetragonal phase to the coexistence of the tetragonal and rhombohedral phase, then to single rhombohedral phase, with an increase of Zr/Ti ratio. Namely, it approaches the morphotropic phase boundary (MPB), when Zr/Ti ratio is 50/50. Figure 4 shows d_{33} as a function of Zr/Ti ratio. The variation of d_{33} is in accordance with the result of k_p.

3.3 Dielectric properties

Figure 5 shows Zr/Ti ratio dependence of ε_r and $tan\delta$ at room temperature. Value of ε_r and $tan\delta$ increased with increasing the Zr/Ti ratio, however, the further increase of Zr/Ti ratio above 50/50 led to gradual reduction of ε_r and $tan\delta$. When Zr/Ti ratio is 50/50, value of ε_r and $tan\delta$ show the maximum values of 2100 and 0.006, respectively. Dielectric constant of PNW–PMS–PZT piezoelectric ceramics with Zr/Ti ratio of 50/50 is 3 times larger than one of PMS–PZT piezoelectric ceramics. There are two possible reasons for the increase of ε_r. First and foremost, PNW with high ε_r was added into PMS–PZT ceramics. Second, Curie temperature of PNW–PMS–PZT ceramics moved towards lower temperature side owing to PNW with lower Curie temperature added. Figure 6 shows Zr/Ti ratio dependence of Curie temperature of PNW–PMS–PZT ceramics. With increasing of Zr/Ti ratio, the Curie temperature of PNW–PMS–PZT ceramics becomes lower, this is due to the decrease of amount of $PbTiO_3$ that has the relative high Curie temperature of 495 °C [12].

Since the piezoelectric transformer operate at its resonant frequency in transformation between electrical and mechanical energy, the properties of piezoceramic materials should combine a high mechanical quality factor Q_m with high electromechanical coupling factor k_p [13, 14].Take into consideration the values of ε_r, $tan\delta$, k_p and Q_m, it can be concluded that the composition with Zr/Ti ratio of 50/50 can be suitable for high-power piezoelectric transformer.

4 Conclusion

PNW–PMS–PZT ceramics of pure perovskite structure were prepared by traditional ceramics process. The phase structure of system was transformed from tetragonal to rhombohedral with an increase of Zr/Ti ratio. The composition containing Zr/Ti ratio of 50/50 gave the desirable piezoelectric properties, i.e. ε_r=2100, $tan\delta$=0.006, k_p=0.613, Q_m=1300, d_{33}=380pC/N and T_c=205 °C, which makes this materials a good candidate for high-power multilayer piezoelectric transformer applications.

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